

Low Field NMR

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1 Introduction

Nuclear magnetic resonance (NMR) is a method for studying the composition of substances. It offers information on the chemical structure, conformation and dynamic properties of molecules [1]. The traditional instrumentation is bulky and due to the use of cryogenics and strong magnets, a safety concern. The instrumentation is expensive and require regular filling of the cryogenics, which makes the operating costs of these machines substantial. These restrictions make the use of NMR less convenient, since the samples need to be transported to a remote laboratory for an analysis, rather than making the analysis on the go.

Recently the trend of making technology smaller and more convenient has been seen also in NMR instruments. With the use of lower magnetic fields and frequencies, the instruments can be made so compact, that even tabletop NMR devices are getting more common. These new compact instruments have been introduced on the side of the traditional spectrometers to make NMR more accessible, and to take some of the workload off from the traditional spectrometers. Tabletop instrumentation is also supposed to be easier to use, and they could be operated by non-professionals for the basic analysis. They are also an interest to the scientists, since the low field NMR opens up new possibilities for experiments. These low field variants also require little to no maintenance [2].

The disadvantage of NMR at low fields is the lower sensitivity due to the smaller differences of the populations of the spin states. This can be overcome with the use of different hyperpolarization methods or different detection methods that are more sensitive at the used precession frequencies [3]. The signal to noise ratio is also usually lower, leading to the need of longer acquisition times.

Some of these low field NMR devices are mobile and therefore can be operated outside the laboratory. This opens up new possibilities for the use of NMR for industrial and commercial uses. The low field NMR is used for monitoring, basic laboratory experiments and process controlling in the food industry [4, 5].

2 Basics of NMR

The following theory is based on sources [6, 7, 8]. NMR is a phenomenon, which occurs when atoms, with nuclei that possess a property called spin, are placed in a static magnetic field and then exposed to a second oscillating magnetic field.

2.1 Spin

Spin is a property that protons, electrons and neutrons possess. For some nuclei, such as ^1H and ^{13}C , the spin of protons or neutrons is unpaired. These unpaired spins are of interest in NMR. If a particle has a spin angular momentum, \mathbf{J} , then it also has a magnetic moment, $\boldsymbol{\mu}$, characterised by spin angular momentum and the gyromagnetic ratio γ . The gyromagnetic ratio is characteristic to each nucleus.

$$\boldsymbol{\mu} = \gamma \mathbf{J} \quad (2.1.1)$$

Unpaired nucleus has the spin angular momentum, which has a magnitude

$$|\mathbf{J}| = \sqrt{I(I+1)}\hbar \quad (2.1.2)$$

where I is the spin quantum number. From quantum mechanics, we know that the property spin I comes in multiplets of $1/2$ and therefore the spin angular momentum as well as the magnetic moment are quantized. Now the length of the magnetic moment vector is

$$|\boldsymbol{\mu}| = \gamma \sqrt{I(I+1)}\hbar \quad (2.1.3)$$

In a magnetic field, these spins act like tiny magnetic dipoles, orienting towards the static magnetic field they are kept in. The spins can orient in configurations with lower energy or higher energy. The higher energy state can be achieved, when the lower state absorbs a photon. In a static magnetic field a spin can absorb a photon with a frequency of ν , which depends on the gyromagnetic ratio γ and the magnetic field B .

$$\nu = \frac{\gamma}{2\pi} B \quad (2.1.4)$$

The difference between the higher and lower energy states is dependent on Planck's constant h and the frequency ν , which is also called the Larmor frequency.

$$E = h\nu = \frac{h\gamma}{2\pi}B \quad (2.1.5)$$

2.2 Interactions

2.2.1 Zeeman effect

Without an external magnetic field, the spins are oriented in all possible directions, meaning that there's no bulk magnetization caused by the spins. However, as mentioned before, the spins act like small magnetic dipoles causing them to orient towards the external field they are placed in.

There are two possible observable orientations for a spin 1/2 nucleus: to orient parallel or antiparallel to the field. These orientations are called α and β respectively. From quantum mechanics, we get that the energies of these states are characterized by quantum number m that can get values from I to $-I$. For a spin 1/2 nucleus, those values would be +1/2 and -1/2, which are the two possible energy states for a spin 1/2 system. This splitting is called the Zeeman splitting. The energy difference between these two states is

$$\Delta E = \hbar\gamma B \quad (2.2.1)$$

From this equation we can see that the Zeeman splitting is proportional to the applied magnetic field. As the strength of the magnetic field increases the difference in energy between the states α and β increases as shown in the Figure 1 below.

At high field the Zeeman effect is the dominating interaction leading to a simple spectrum. When an intermediate field is used the spectrum is most complicated as the Zeeman effect and other interactions are of the same magnitude.

2.2.2 Spin-spin coupling

Nuclei that are in the same chemical environment are called equivalent and those in different chemical environment are called nonequivalent. Nuclei that are close to each other affect the magnetic field that the other experiences. When nonequivalent nuclei are close to each other this effect on the magnetic field is observable and seen in the spectra as splitting of the peaks. This is called spin-spin or J coupling. J coupling is important tool for analyzing

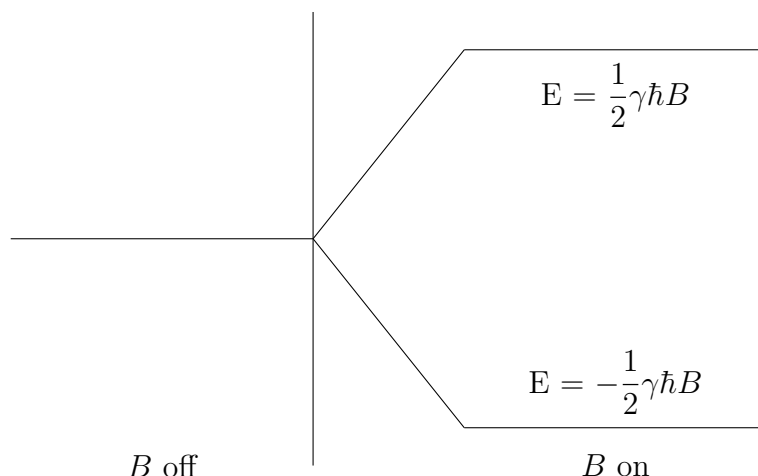


Figure 1: Zeeman effect when the magnetic field B is turned on and off.

the structure of molecules and it is typically the dominating interaction in ultra-low fields.

2.2.3 Chemical shift

In a magnetic field, the electrons of an atom circulate around the B_0 field. This causes a small magnetic field that affects the magnetic field at the nucleus. The field at the nucleus is therefore smaller than the applied B_0 by a factor of σ .

$$B = B_0(1 - \sigma) \quad (2.2.2)$$

The factor σ varies for different parts of the molecule due to the different chemical environments. The difference between the resonances of the chemical environments is called the chemical shift. The resonance frequency of nuclei depend on the strength of the applied magnetic field. Therefore, it would be difficult to compare measurements from different magnetic fields. To overcome this issue the chemical shift is compared to a reference frequency. This is done by using the difference between the resonance frequency and a frequency of a standard divided by the standard. For proton and carbon the standard used is usually tetramethylsilane ($\text{Si}(\text{CH}_3)_4$) or TMS for short. Chemical shift is denoted with the symbol δ and is given in the units of parts per million (ppm).

$$\delta = \frac{(v - v_{REF})}{v_{REF}} \times 10^6 \quad (2.2.3)$$

2.3 Relaxation

The net magnetization is parallel to the external magnetic field and this component is called the longitudinal component of the magnetization. The time that describes the time for the net longitudinal component of the magnetization M_z to return from a flipped state to its equilibrium is called the spin-lattice relaxation time which is usually given the symbol T_1 . T_1 is characterized by the function

$$M_z = M_0(1 - e^{-t/T_1}) \quad (2.3.1)$$

where M_0 is the net magnetization and t is the time after the flip of the magnetization. Spin-lattice relaxation time constant T_1 is the time it takes for the net magnetization to return towards the longitudinal equilibrium by a factor of e , which is a mathematical constant that is equal to approximately 2.71828.

The net magnetization of the sample consists of groups of spins in different chemical environments. These different groups experience a fractionally different magnetic field and therefore rotate at their own Larmor frequency. This causes the net magnetization to dephase. Spin-spin relaxation time constant T_2 is used to describe the change of the transverse magnetization M_{tr} . This process is described by the function

$$M_{tr} = M_{tr0}e^{-t/T_2} \quad (2.3.2)$$

where M_{tr0} is the value of the magnetization at $t=0$ and t is the time after the flip of the magnetization. T_2 is the time it takes for the transverse magnetization to decay by a factor of e .

2.4 Net magnetization

As mentioned before the spins in a magnetic field have a net alignment with the external magnetic field. There populations of the two different states, α and β are different. According to Boltzman statistics the ratio of the nuclei in the different orientations is

$$\frac{N_{+1/2}}{N_{-1/2}} = e^{-\Delta E/kT} \approx 1 - \frac{\Delta E}{kT} = 1 - \frac{\gamma \hbar B}{kT} \quad (2.4.1)$$

where N is the number of spins in that state, ΔE is the energy difference between the two states, k is Boltzman constant and T is the temperature. Now the relative difference between these states is

$$\frac{N_{+1/2} - N_{-1/2}}{N_{+1/2} + N_{-1/2}} \approx \frac{\Delta E}{2kT} = \frac{\gamma \hbar B}{2kT} \quad (2.4.2)$$

When all the magnetic moments of the sample consisting of N nuclei are taken into account, a net magnetization parallel to the external magnetic field is [8]

$$M_0 = \frac{N\gamma^2 \hbar^2 I(I+1)}{3kT} B \quad (2.4.3)$$

2.5 Signal acquisition

To detect the signal, the spins are manipulated. This is done using a radio frequency (rf) pulse and a coil. The rf pulse is used on a frequency that matches the Larmor frequency of the nucleus that is studied. The spins precess around the direction of the external magnetic field. When the pulses are used on the correct frequency, the orientation of the spin can be flipped using low power pulses. The coil is placed around the sample, and when a pulse is given to the coil, it creates a magnetic field B_1 in the direction perpendicular to the external magnetic field. This causes the spins to orient towards the B_1 plane. The rotation angle can be calculated from the equation

$$\theta = \gamma B_1 \tau \quad (2.5.1)$$

where γ is the gyromagnetic ratio that was mentioned already, τ is the time of the pulse and B_1 is the magnetic field generated by the rf coil. After the flip the system will return towards equilibrium, with the net magnetization precessing around the external magnetic field with the Larmor frequency.

This rotating net magnetization induces a voltage to a detection coil, placed around the sample. The detection will be discussed later. The signal from the detection coil is called the free induction decay (FID) and it is amplified with a preamplifier and sent to the console for analysis. The signal

is Fourier transformed using a computer to transform the FID into frequency domain, which will show the chemical shift of different spins of the molecule.

2.6 Fourier transform

Fourier transform is used to transform functions from time domain to frequency domain and an inverse Fourier transform does the opposite [6]. The Fourier transform is defined by [9]

$$f(\omega) = \int_{-\infty}^{\infty} f(t)e^{-i\omega t} dt \quad (2.6.1)$$

The induced FID consists of many frequencies and when Fourier transformed, the distribution of frequencies is received. The transformation gives Lorentzian lines for each of the different frequencies in the sample.

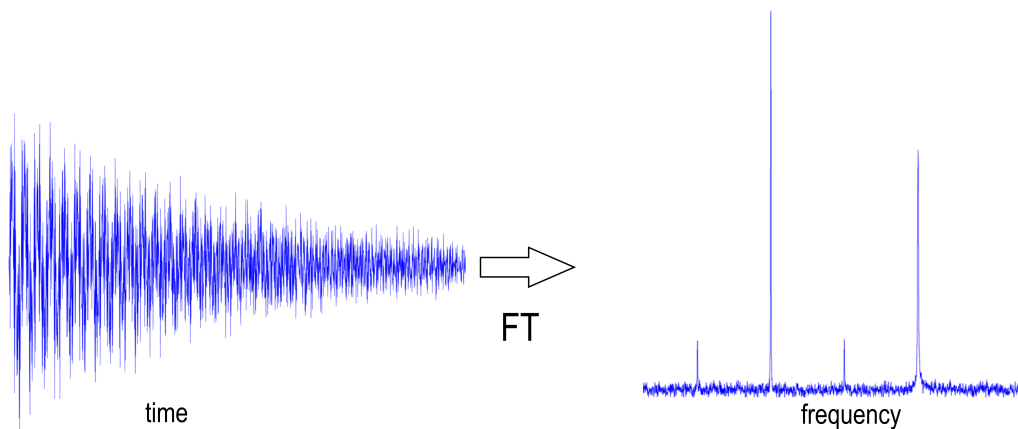


Figure 2: FID Fourier transformed to frequency domain.

The Fourier transform is an essential tool for NMR. From the FID it is impossible to tell the different frequencies detected.

3 NMR instruments

3.1 Traditional NMR instruments

Traditional NMR instruments consist of three main components: magnet system, console and operating console [12]. The operating console is a computer

that is used to control the whole system thoroughly. On the computer is the software to control the console and to store and analyze received data. The operator console is attached to the console that is used to operate the magnet system. In the console, there are amplifiers that are used to give the needed pulses to the rf coils located in a probe. The console is used to control the temperature of the probe, to shim the magnetic field, tune the probe circuit and receive and amplify the received signal. A probe is a device that is used to excite the spins and to detect the signal. It is inserted in the middle of the magnetic field and the sample is placed inside it. The excitation of the spins is done using the rf coils located in the top of the probe. The probe also contains the needed hardware for adjusting the temperature of the sample. The probe is a part of the magnet system that consists of the magnet and its dewar, shim coils pre-amplifier and the probe. The magnet is used to get a strong homogeneous magnetic field over the measured volume of the sample. To detect the signal, this magnetic field must be homogeneous enough. A process called shimming is used to adjust the magnetic field as needed. Shimming is done using additional coils, called shim coils. In traditional systems the magnetic field is produced using a superconducting magnet that is kept at low temperatures by submerging it in liquid helium which is surrounded by liquid nitrogen. These cryogenics are stored in dewars inside the magnet system, in a vacuum chamber. The nitrogen is used to keep the evaporation of the helium low. The refill of these liquids is done using the ports on top of the magnet system.

3.2 Low-field variant

There are different approaches to using NMR in low fields. Modern permanent magnets or magnet arrays are commonly used in the low field NMR instruments to generate a homogeneous enough field over the sample area. Halbach arrays and electromagnets are a way of producing a quite homogeneous field with ease. The principle of these instruments is fundamentally the same as with the high-field variants but they utilize lower resonance frequencies. Low field NMR fields range from no external magnetic field to around one tesla range. NMR can be done using only the Earth's own magnetic field whose intensity range is from 25 microtesla to 65 microtesla. The problem with Earth's magnetic field is that it drifts leading to longer acquisitions getting inaccurate. Meanwhile the intensity of the magnetic field would require long acquisition times to get sufficient data. NMR in Earth's

magnetic field has been done successfully [10, 11] but usually low field NMR is done using more powerful external magnets. The low-field NMR instruments may be designed to be mobile. This requires the magnet system to be as compact as possible while still yielding magnetic fields strong enough for the measurements that will be conducted.

3.2.1 Halbach array

Halbach arrays consist of smaller permanent magnet segments oriented in such way that the magnetic field in the middle of the array is homogeneous [13]. Usually, to increase the homogeneity, a number of segments are used. A problem with the Halbach arrays is that the magnetic field is low and the inhomogeneity in the magnets forming this array need to be minimized. These magnets are usually also temperature dependent, which means that they need to be operated in a stable temperature. In addition, the Halbach array needs to be shimmed daily with a reference sample and shim coils or separate permanent shimming magnets. The instability of the magnetic field is an issue when measuring over long periods and averaging these measurements together. Other disadvantages are the low sensitivity caused by the low magnetic field and low signal to noise ratio (SNR). The benefit of Halbach arrays is an open access design, which allows bigger samples to be analyzed. The changing of the sample is also a simple procedure. The sample can also be observed and studied while inside the magnet. This is a significant benefit when substances with rapid changes are studied. Furthermore, the cost of the Halbach arrays is a fraction of the traditional cryogen cooled magnet. The Halbach arrays are used all the way to $B_0 = 1$ T which corresponds to 42,5 MHz for ^1H [4].

3.2.2 Helmholtz coil

Helmholtz coils are also used to produce the magnetic field necessary for NMR[14]. The Helmholtz coils consist of two identical coils with radius R . The coils are placed a distance equal to the radius apart from each other. Each of these coils induce a magnetic field due to the current that is fed to the wire that the coils are made of. The magnetic field B_m in the middle of the coils can be calculated from the equation derived from Biot-Savart Law

$$B_m = \frac{8}{5\sqrt{5}} \frac{\mu_0 n I}{R} \quad (3.2.1)$$

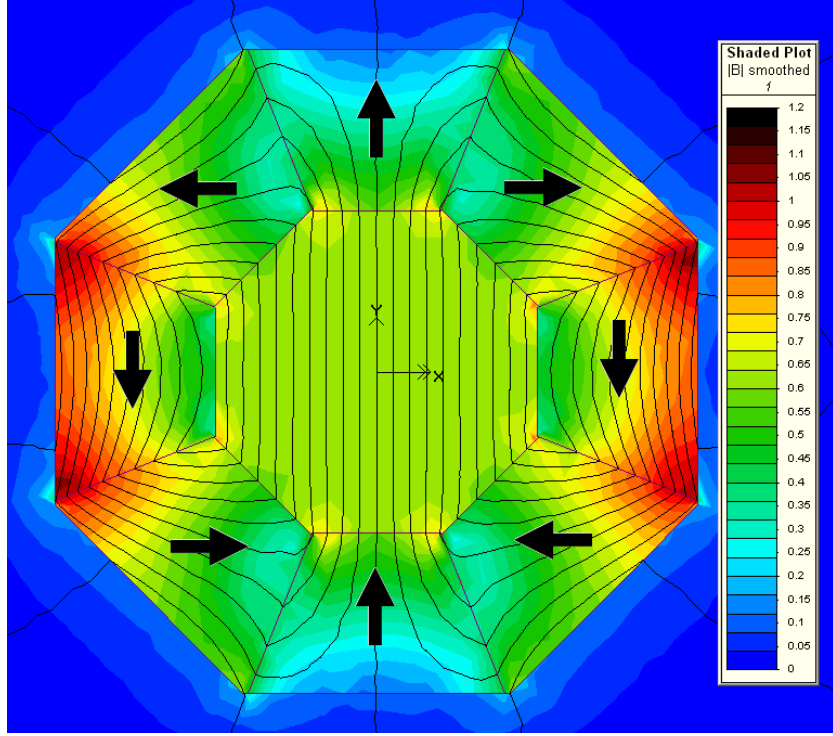


Figure 3: Magnetic field generated by Halbach array. source: Wikimedia commons, created by Zureks, 2008, <https://commons.wikimedia.org/wiki/File:HalbacharraybyZureks.png>

where μ_0 is the vacuum permeability, n is the number of turns in the coils, I is the current fed to the coils and R is the distance between the two coils. The magnetic field produced by these coils is homogenous in the center but sometimes additional coils are added to improve homogeneity.

3.2.3 Permanent magnets

Modern permanent magnets are usually made of neodymium iron boron (Nd-FeB) or samarian-cobalt (SmCo). The permanent magnets can be used individually or in various arrangements. The two main designs for tabletop NMR devices are the Halbach array and a design with two magnetic poles mounted to an iron yoke [4]. The two-pole design can be an open U magnet, or a closed design with an additional yoke fixed to the top. This gives the opportunity for an open access NMR device. The additional yoke is used to

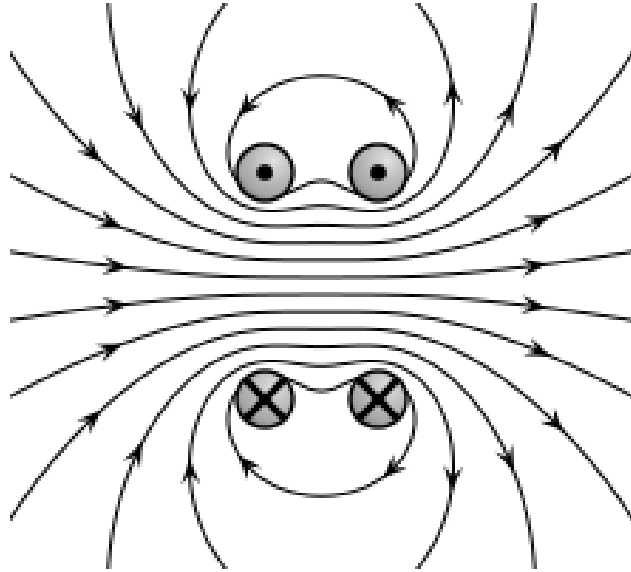


Figure 4: Magnetic field generated by Helmholtz coils. Source: Wikimedia commons, created by Geek3, 2010, <https://commons.wikimedia.org/wiki/File:VFPhelmholtzcoilthumb.svg>

get a closed geometry leading to more homogenous magnetic field. The magnetic field of these materials are temperature dependent and therefore they are operated at a higher temperature compared to ambient, usually at 35-40 degrees Celsius. The stability can be improved by using a large thermal mass with the magnets. SmCo and NdFeB, as well as other materials with different thermal coefficients, are often fused into the same magnet to get a less temperature sensitive magnet. With permanent magnets, the homogeneity of the field can be enhanced with the addition of shim coils if needed. The problem with these shim coils is that they often require significant power and will generate heat leading to magnet field drift. With permanent magnets a field strength of over 1.5 T can be achieved [4], but it requires a significant addition to the volume of the magnetic material.

3.3 Detection

The detection of signal is done using a radio frequency resonant circuit consisting of inductors, capacitors and resistors. The components are chosen to match the wanted detection frequencies. The coils are usually made of

copper wires of different sizes and lengths that are wound to either solenoids or other types of coils such as saddle coils.

3.3.1 Induction

The following theory is based on the lecture notes of electromagnetism[15]. The magnetic flux Φ_B through a wire loop is given by the formula

$$\Phi_B = \int_S \mathbf{B} \cdot d\mathbf{S} \quad (3.3.1)$$

where \mathbf{S} is the area of the wire loop and \mathbf{B} is the magnetic field. The dot product $\mathbf{B} \cdot d\mathbf{S}$ is the amount of flux passing through the loop. According to the Faraday's law of induction, when the flux passing the loop changes there's an electromotive force denoted with ε acting on the loop. This force is dependent on the change of magnetic flux.

$$\varepsilon = -\frac{d\Phi_B}{dt} \quad (3.3.2)$$

This is the electromotive force (EMF) acting on a single loop of wire. From these equations we can see that the force changes if

- the magnitude or the direction of \mathbf{B} changes
- the area \mathbf{S} of the loop changes or the direction of the \mathbf{S} vector changes.

The induced voltage U_{ind} can be written as

$$U_{ind} = -\frac{d\Phi_B}{dt} = \varepsilon \quad (3.3.3)$$

If the amount of loops is increased there's a voltage induced in each of the loops. These voltages are added since the loops are in series. Now for n loops the induced voltage is

$$U_{ind} = -n \frac{d\Phi_B}{dt} \quad (3.3.4)$$

The inductance L of a loop is the derivative of magnetic flux

$$L = \frac{d\Phi_B}{dI} \quad (3.3.5)$$

Using the Faraday's law we get that the induced voltage is

$$U_{ind} = -L \frac{dI}{dt} \quad (3.3.6)$$

For an air filled solenoid with n turns for a unit of length the magnetic field $B = \mu_0 n I$. The magnetic flux through a single loop is the magnetic field times the area which is $B \pi r^2$. For a solenoid of length l the number of turns is nl and if assumed that the flux going through each loop is the same the flux going through the solenoid is $\Phi_B = \mu_0 n^2 \pi r^2 l I$ and therefore the inductance will be

$$L = \frac{d\Phi_B}{dI} = \mu_0 n^2 \pi r^2 l \quad (3.3.7)$$

Practically, these formulas yield slightly incorrect results as the magnetic field at the ends of the solenoids might vary and commonly this formula of an ideal solenoid is inaccurate.

3.3.2 Detection circuit

To detect the magnetization, a coil is wound and placed around the sample. The coil is placed in the homogenous part of the magnetic field generated by the magnets described above. The coils are usually wound from different gauges of insulated copper wire. In the low field NMR instruments solenoids are a common type of coil, but saddle coils are also used. The coils are designed to have maximum inductance with low resistance leading to maximum signal. The detection circuit is similar to the high field variant but as the frequencies used are of lower magnitude, the exact matching of the impedance isn't as important. The preamps and other equipment are usually 50 Ω impedance, so the circuit is designed to have similar impedance. A simple circuit which consists of matching capacitor C_m and tuning capacitors C_t as well as an inductor L which in this case is the solenoid. Sometimes an additional coil is used to increase the inductance of the circuit.

The angular frequency of the resonance of this circuit can be calculated from the formula

$$\omega = \frac{1}{\sqrt{LC}} \quad (3.3.8)$$

where L is the inductance of the coil used, C is the capacitance of the circuit and ω is the angular frequency. This formula does not take into account the

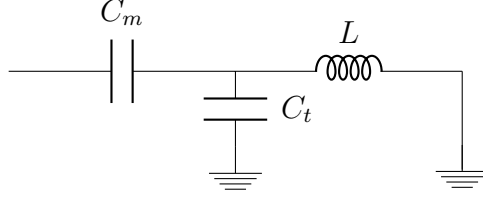


Figure 5: A circuit diagram of a detection circuit for NMR.

resistance of the coil or the other components of the circuit but it gives a good approximation. The resistance can also be taken into account, but the exact resistance of the components, wires and connections between them are difficult to estimate. The capacitors chosen for the circuit can be tunable to compensate for the estimate made here. Now if the inductance of the coil is known, the capacitance of the circuit needed can be calculated. To match the impedance of the circuit to $50\ \Omega$, the matching and tuning capacitors are used. The size of each of the capacitors can be calculated from the equations [16]

$$C_t = \frac{1 - \sqrt{\frac{R_{res}}{50\Omega}}}{\omega_0^2 L} \quad (3.3.9)$$

and

$$C_m = \frac{\sqrt{\frac{R_{res}}{50\Omega}}}{\omega_0^2 L} \quad (3.3.10)$$

where R_{res} is the impedance of the circuit used at resonance and ω_0 is the desired angular frequency.

The spins of the sample are manipulated with an rf pulse to receive a signal. The manipulation of spins requires high power pulses that could harm the preamplifiers used. The high voltage pulse induces a magnetic field when sent to the coil and this current must not reach the preamplifiers. In addition, the signal induced by the flip of the spins must reach the preamplifiers for analysis. This is doable using a separate coil but usually both the detection and manipulation is done using the same coil. This can be accomplished using a transmit/receive (T/R) switch. The T/R switch is usually an active

component, but a passive implementation is also viable. This is achieved with a circuit that consists of crossed diodes that conduct the high voltage away from the sensitive preamplifiers and π network that is used to match the impedance of the switch to $50\ \Omega$.

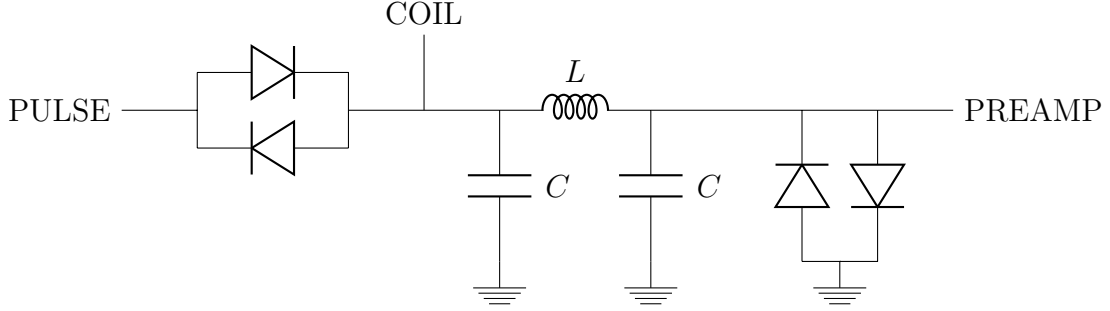


Figure 6: The basic circuit of a T/R switch using π network and crossed diodes.

4 A low-field experimental instrument

The following section is a brief description of the setup I was involved with.

4.1 Experimental set-up

The detection circuit was designed to be as simple as possible, with the opportunity to upgrade later. The circuit is built as shown and described in Figure 5. The detection circuit consists of a coil wound around a flow-through glass cell using a AWG 30 insulated copper coil wire. An auxiliary coil was wound to increase the inductance of the circuit. This was used for smaller sample sizes but for the coil described here it is not necessary. Different types of coils were tested to find the optimal configuration for the cell used. The theoretical inductances were calculated beforehand using an approximation, but the solenoids wound were not ideal leading to slight variation between the theoretical and the measured inductances.

The coil is placed on a holder in the middle of Helmholtz coils. The Helmholtz coils are powered by the amplifiers seen in Figure 8a. The Helmholtz coils are used to create switching magnetic fields B_0 and B_1 . The magnetic

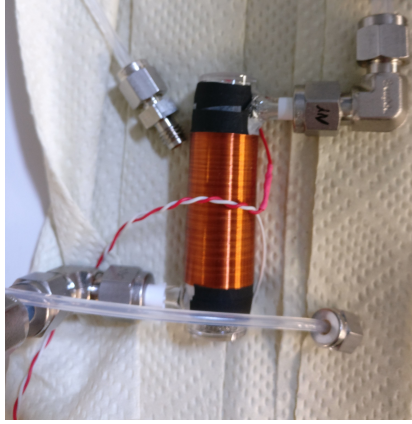


Figure 7: The detection coil wound around a glass cell.

field B_0 is switched on and off on a certain frequency by adjusting the voltage going to the coils and was switching at a rate of 1 Hz for the experiments conducted. The B_1 field, perpendicular to the B_0 field, is switching at the resonance frequency of the detection coil. The polarization of the sample is achieved using a traditional high field 14 Tesla magnet. A polarizer, which is a container made of teflon, is filled and put in to the magnetic field. The polarizer is connected to the detection cell using tubing and fittings. A pump is used to transport the sample between the magnet and the detection cell. The length of the tube between the polarizer and the cell is minimized for faster transportation. This is done to reduce the relaxation before detection to maximize the signal induced. The pumping speed can be adjusted to reduce the relaxation time as well. The pumping is causing vibrations and bubbles to the cell leading to more noise detected.

The detection circuit was designed to work for multiple coils. The target frequency was set to be around 20-25 kHz and the components were chosen accordingly. The inductance of the coil was estimated, measured and confirmed from the resonance frequencies that were measured using a set of known capacitors. The resonance frequency of the circuit was determined by giving the B_1 field a sweep of frequencies. The response of the circuit was measured and the resonance frequency was determined from the data gathered. The estimated capacitors for the frequency wanted were calculated and placed on a breadboard for testing. The circuit was tweaked using slight variations of capacitors until the desired frequency was found. The

components were enclosed in a box seen in Figure 8a.

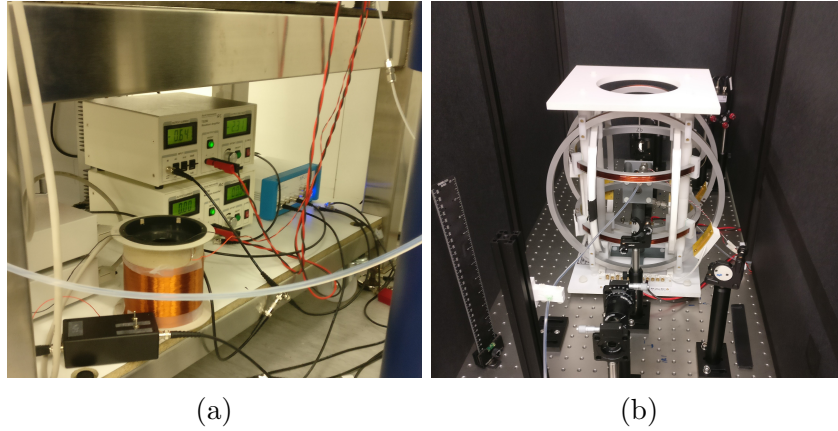


Figure 8: (a): Amplifiers and the detection components enclosed in a box. (b): The detection coil in a holder inside the Helmholtz coils.



Figure 9: The setup next to the polarizing magnet system.

The software used for controlling the amplifiers as well as to analyze the signal was programmed using LabVIEW.

4.2 Experiments

A set of experiments was conducted to ensure that the designed circuit works at the desired frequency and to demonstrate the theory described. The first experiment was to test the effects of the components of the circuit. This was done to verify that the components planned would yield the desired detection frequency and to optimize the circuit to detect as much signal as possible. A set of different capacitors and frequencies were used to see the response of the circuit and the induced current was examined. In addition to these tests, two experiments were conducted to demonstrate the theory. A pumping speed test was run to see the effects of the transfer time on the induced signal and to demonstrate the relaxation process. The second experiment was conducted to see the effect of the applied B_0 field and to demonstrate the frequency dependence on the magnetic field.

4.3 Results

Experiments were conducted using water (H_2O). The coil was wound around a flow-through glass cylinder with 15 mm outer diameter and 70 mm length. Four layers of AWG 30 copper wire with approximately 140 turns per layer (560 altogether) were used. The inductance of the coil was measured to be 1.139 mH with a resistance of 8.6 Ω . The resonance of the circuit was studied using frequencies from 1 kHz to 50 kHz. The data was gathered and analyzed in Excel. A set of sweeps is plotted in Figure 10. These plots are from an older cell, with 1.186 mH inductance and 8.6 Ω resistance, and are shown for demonstrative purposes. The capacitors used for these plots are listed in Figure 10. As seen from the figure, the best combination was found to be 29.4 nF as a matching capacitor and 20 nF as a tuning capacitor. With these capacitors, the peak is the sharpest and has the highest current. The theoretical values were calculated to be 31.3 nF as tuning and 18.7 nF for matching. Additional tuning could be done but the increase to the induced signal is insignificant. The resonant frequency of the used circuit was determined to be 21.05 kHz and the sweep of this circuit is plotted in Figure 11.

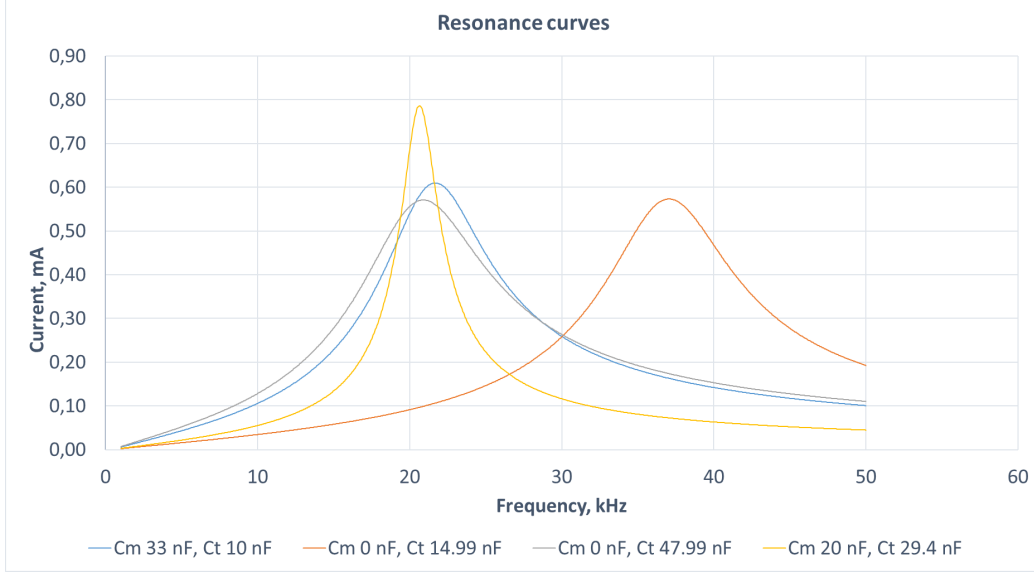


Figure 10: Resonance curves of the circuit using different matching and tuning capacitors. These curves are plotted from the data gathered from an older cell with 1.186 mH inductance and 8.6Ω resistance. The effect of the matching and tuning capacitors can be seen from these plots. A nonoptimal pair of capacitors results in a broad curve with lower peak current.

The effects of the pumping speeds on the decay of the intensity were studied using a Masterflex L/S model 07528-30 pump. The pumping speeds used were from 10 to 100 percent speed with increments of 10. Two measurements of 250 seconds were conducted with each speed and the results were averaged. Due to the switching B_0 field, a peak was detected at 1 Hz. The intensities of the averaged peaks are listed in Table 1

The volume of the transfer tube and half of the cell was measured. As the pumping speed is known, the transfer time from the polarizer to the middle of the cell can be calculated. These times and the intensities corresponding to each time are plotted in Figure 12. According to the theory of relaxation, the decay of the intensity over time should be exponential. A trendline was fitted to the data gathered and as expected an exponential decay was observed. The relaxation time of protons in water calculated from the equation fitted to the decay is approximately 3 s.

The effects of the switching field were studied using different voltages fed to the Helmholtz coils. The used voltages used for the B_0 field ranged from

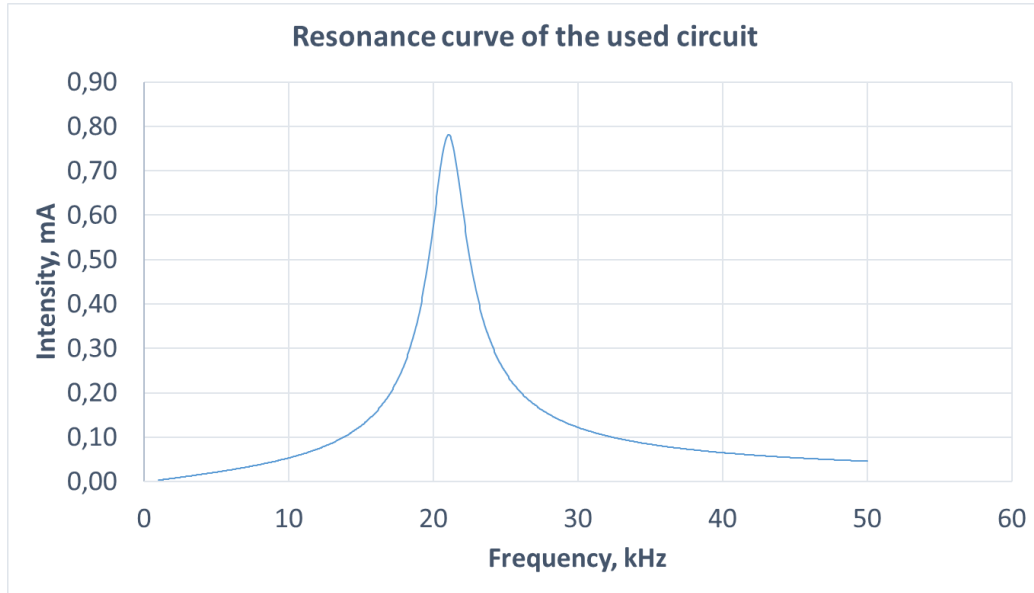


Figure 11: The resonance curve of the used circuit. The resonance frequency determined from this plot is 21.05 kHz.

Table 1: The intensities of the peaks with different pumping speeds.

Pumping speed	Intensity, A
10	$1.71 \cdot 10^{-9}$
20	$3.01 \cdot 10^{-8}$
30	$8.71 \cdot 10^{-8}$
40	$1.58 \cdot 10^{-7}$
50	$2.02 \cdot 10^{-7}$
60	$2.29 \cdot 10^{-7}$
70	$2.35 \cdot 10^{-7}$
80	$3.08 \cdot 10^{-7}$
90	$3.30 \cdot 10^{-7}$
100	$3.44 \cdot 10^{-7}$

-0.25V to -0.15V. This corresponds to magnetic field strengths from 0.3975 mT to 0.5825 mT. The powersupplies used are Accel instruments ts250. One of the powersupplies is feeding DC current to the switching B_0 field, and the other one is used to create a B_1 field which is controlled using a Zurich

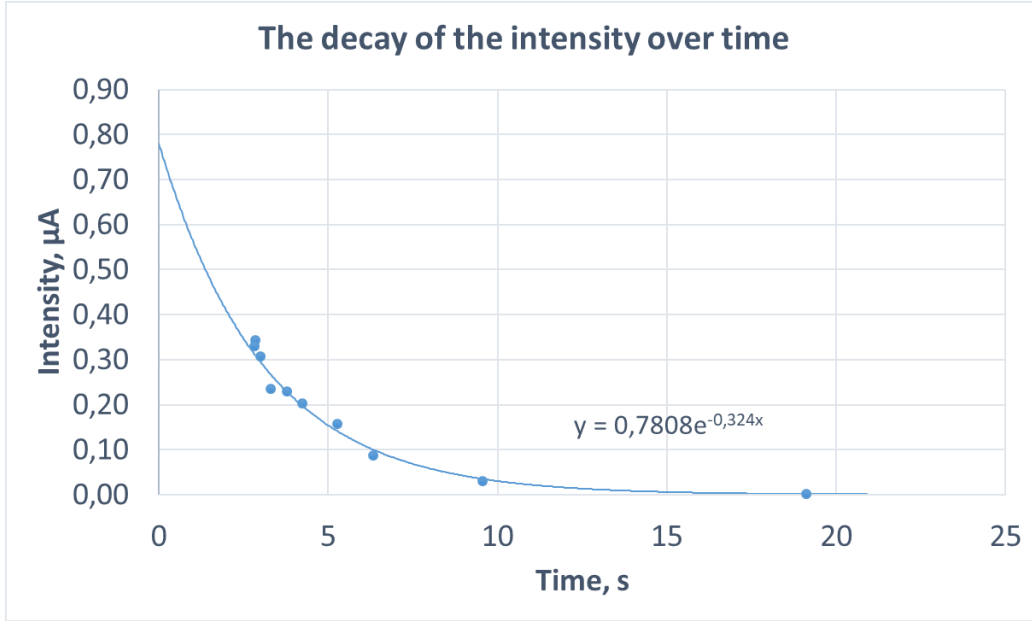


Figure 12: The exponential decay of the intensity of the signal. An exponential trendline is fitted to the data points.

instruments MFLI lock-in amplifier. The voltage affects the magnetic field that is present when detecting the signal. If the magnetic field changes, the Larmor frequency changes and therefore the optimal detection frequency should change. To demonstrate this, the detection frequency was kept the same and the measurements were done using different B_0 magnetic fields.

As expected, the intensity of the peaks varies as the magnetic field changes. These intensities are plotted in Figure 13. The highest intensity is observed at -0.20V voltage corresponding to 0.49 mT. At this voltage the Larmor frequency in the generated magnetic field matches with the detection frequency. When the voltage is shifted, less and less signal is obtained.

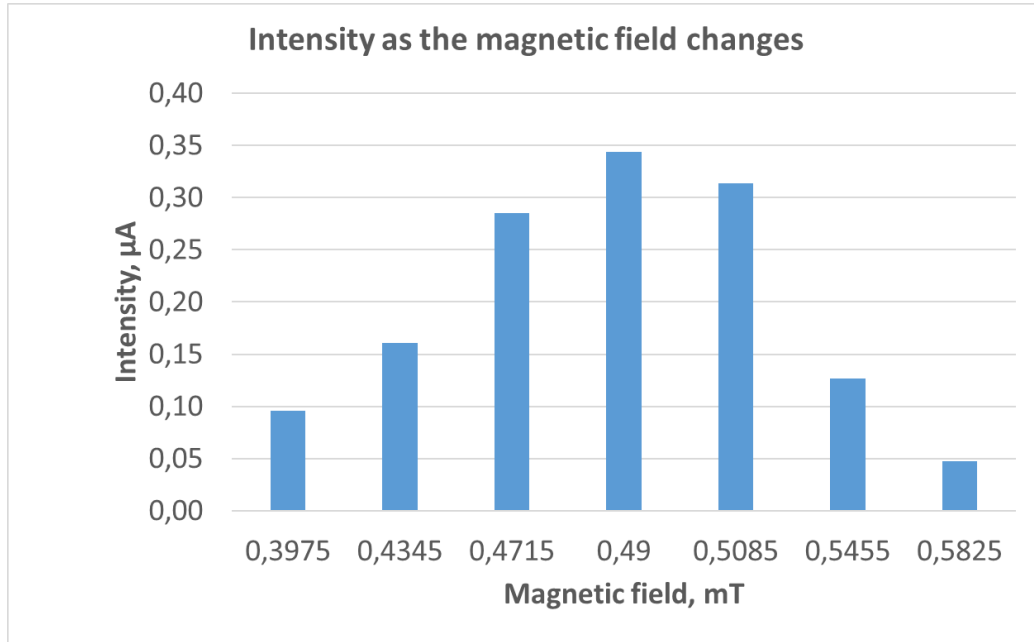


Figure 13: The effect of the magnetic field B_0 used. The intensity of the signal obtained decreases as the magnetic field is shifted away from the optimal field.

5 Conclusions

The trend of making electronics more compact is also seen in NMR. Some of the restrictions and problems, such as the use of cryogenics and the size of the instruments, of traditional NMR instrumentation are solved using low fields. The instruments are compact and desk-top NMR instruments are becoming common for the basic analysis. The magnet system can be made compact and homogenous enough using modern permanent magnet arrays or electromagnets. The permanent magnets can also be used in combination with shim coils to increase the homogeneity of the field. Magnet arrays such as the Halbach array are capable of producing magnetic fields up to 1.5 T. The drawback of producing such high magnetic fields is the increase in the volume of the magnetic material. The fields produced are homogenous enough for conducting NMR experiments. These magnets require little to no maintenance which is an advantage over the traditional instrumentation that require filling of cryogenics constantly. The cost of such magnetic systems are substantially lower than the high field ones.

A low field NMR instrument detection circuit was designed and constructed. The detection circuit was designed to be used at around 20-25 kHz. A coil was wound around the sample cell and the circuit was tuned to yield the highest induced current. Some experiments were conducted to demonstrate the theory described and to show that the built instrument is functional. A pumping speed test was performed to see how the transfer time of the sample affects the acquired signal. The experiment yielded the expected exponential decay of the signal as the time of transportation increased. Also, to demonstrate the effect of the used B_0 field, the magnetic field was changed using different voltages fed to the Helmholtz coils. The prediction was that the Larmor frequencies in the fields generated by these coils would not match the detection frequency if the voltage was altered. The experiment shows that this prediction is true as the induced signal decreased when detected in non optimal fields.

References

- [1] K. Singh, B. Blümich: *NMR spectroscopy with compact instruments*, Trends in Analytical Chemistry 83 (2016) 12-26, Doi 10.1016/j.trac.2016.02.014
- [2] B. Blümich: *Introduction to compact NMR: A review of methods*, Trends in Analytical Chemistry 83 (2016) 2-11, Doi 10.1016/j.trac.2015.12.012
- [3] B. Blümich et al.: *NMR at low magnetic fields*, Chemical Physics Letters 477 (2009) 231-240, Doi 10.1016/j.cplett.2009.06.096.
- [4] J. Mitchell, L.F. Gladden, T.C. Chandrasekera, E.J. Fordham: *Low-field permanent magnets for industrial process and quality control*, Progress in Nuclear Magnetic Resonance Spectroscopy 76 (2014) 1-60, Doi 10.1016/j.pnmrs.2013.09.001.
- [5] F. Dalitz, M. Cudaj, M. Maiwald, G. Guthausen: *Process and reaction monitoring by low-field NMR spectroscopy*, Progress in Nuclear Magnetic Resonance Spectroscopy 60 (2012) 52-70, Doi 10.1016/j.pnmrs.2011.11.003.
- [6] J. P. Hornak: *The Basics of NMR*, <https://www.cis.rit.edu/htbooks/nmr/inside.htm> May 2019
- [7] J. Keeler: *Understanding NMR Spectroscopy*, Wiley-Blackwell; 2nd edition (13 April 2010)
- [8] V. Telkki: *Lecture notes for NMR Spectroscopy*, 2018
- [9] A. Pinsky, Mark: *Introduction to Fourier Analysis and Wavelets*. Brooks/Cole, 2002
- [10] Carl A Michal: *A low-cost spectrometer for NMR measurements in the Earth's magnetic field*, 2010 Meas. Sci. Technol. 21 105902, Doi 10.1088/0957-0233/21/10/105902
- [11] A. Mohoric, J. Stepisnik: *NMR in the Earths magnetic field* Progress in Nuclear Magnetic Resonance Spectroscopy 54 (2009) 166182, Doi 10.1016/j.pnmrs.2008.07.002.

- [12] S. Bai: *Nuclear Magnetic Resonance Instrumentation* In Encyclopedia of Analytical Chemistry (2008) (eds R. A. Meyers and R. A. Meyers). doi:10.1002/9780470027318.a6108.pub2
- [13] B. P. Hills, K. M. Wright, D. G. Gillies: *A low-field, low-cost Halbach magnet array for open-access NMR*, Journal of Magnetic Resonance 175 (2005) 336-339, Doi 10.1016/j.jmr.2005.04.015
- [14] R. R. A. Syms, M. M. Ahmad, I. R. Young, Y Li, J. Hand, D. Gilderdale: *MEMS Helmholtz coils for magnetic resonance imaging*, Journal of Micromechanics and Microengineering 2005 15 S1, Doi 10.1088/0960-1317/15/7/001
- [15] T. Nygrén, A. Aikio: *Lecture notes on electromagnetism*, 2017
- [16] Anferova, S. and Anferov, V. and Adams, M. and Blmler, P. and Routley, N. and Hailu, K. and Kupferschlger, K. and Mallett, M.J.D. and Schroeder, G. and Sharma, S. and Blümich, B.: *Construction of a NM-RMOUSE with short dead time*, Concepts in Magnetic Resonance, 15 (2002) 15-25, Doi 10.1002/cmr.10013